

## **Low temperature upcycling of polyethylene to gasoline range chemicals: hydrogen transfer and heat compensation to endothermic pyrolysis reaction over zeolites**

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### **Abstract:**

Selective production of gasoline ranged chemicals were of great interest in the field of plastic upcycling. This work reports exothermic hydrogen transfer reaction which was observed when HY zeolite was adopted to catalytic pyrolyze the polyethylene to gasoline ranged chemicals, while it was not observed when H-ZSM5 was used as catalyst. Both zeolite catalysts could significantly bring down the reaction temperature from 500 to 300-350 °C. TG-FITR analysis revealed that products obtained with HY zeolites were dominated with saturated hydrocarbons as compared to H-ZSM5 where the combination of alkanes, alkenes, and aromatics was obtained. In addition to the formation of saturated compounds, the TG-DSC analysis confirmed that, over the HY zeolites, the endothermic hydrogen transfer reaction of olefins occurred along with the pyrolysis of LDPE visibly when the zeolite ratio in the zeolite/polyethylene mixture exceeded 50% by mass. The TG results also indicated that the polyethylene undergone nearly 100% converted with very few residues. Further product analysis from batch pyrolysis by GC-MS confirmed that gasoline ranged iso-alkanes were produced over HY zeolite. This study highlighted that coupling exothermic hydrogen transfer reactions with endothermic pyrolysis

could be an energy-efficient way of producing gasoline ranged chemicals. Chemical upcycling of plastics is tunable by using different zeolite combinations for the formation of desired products.

**Keywords:** Plastic upcycling; Zeolites; Gasoline; Product analysis; Endothermic

## **1. Introduction**

Plastic waste has become a huge environmental concern to the public for decades. Countless plastics were produced for domestic use, but only a slight portion was eventually recycled. Although these plastics were labeled with recyclable signs, only 8.4% used plastics were recycled in 2017 [1]. Unfortunately, some of the waste plastics ended up in the ocean posing an already existed threat toward the marine eco-system. It was estimated that 4.4 to 12.7 million metric tons of waste plastics were dumped into the ocean every year [2]. Recent studies have even shown that these plastics could be consumed by aquatic fishes, turned into micro-particles, and passed on to the human body through the food chain [3,4]. Therefore, the issue of plastic waste must be solved before it is completely out of control.

Plastic upcycling is a new trend for the solid waste treatment. Although the recycling of the plastics has been done under a limited scale and to only certain types of plastics, it is far from enough. The biggest challenge to the plastic recycling remains that the process was not economically feasible, often due to the large capital investment for the technology and high operating cost [5]. Currently, mechanical recycling is still the only widely used technology for treating the waste plastic, but it is only limited to poly(ethylene terephthalate) and polyethylene [6]. Advanced recycling technologies, such as chemical recycling, are highly desirable. The chemical recycling turning one single-stream plastic or multi-plastic mixtures into valuable

platform monomers is a promising upcycling route toward solving the plastic waste issue, despite of the hardship of developing the catalyst with excellent selectivity and efficiency [7].

Waste plastics are great sources to produce fuel or chemical intermediates. These plastics consist of hydrogen and carbon elements, some of which have oxygen or halogen. In the presence of catalyst, the long-chain waste plastics could be cracked into shorter carbon chains which fall into the transportation fuel range. Among these plastics, low-density polyethylene (LDPE) is one suitable candidate for producing hydrocarbons, which could be further upgraded to gasoline or lubrication oil. A non-catalytic pyrolysis between 450-550 °C can convert LDPE to short-chain hydrocarbons. With the help of the catalysts, the temperature could be significantly decreased, thus, reducing the energy input. Many studies have been conducted with zeolites as catalysts for the catalytic conversion of LDPE to short-chain hydrocarbons. Generally, the products from this process included gaseous C<sub>1</sub>-C<sub>4</sub>, gasoline fraction C<sub>5</sub>-C<sub>11</sub>, heavy hydrocarbons C<sub>12+</sub>, and coke [8]. One study found out that the Y zeolite led to a higher oil and less gas products than the non-catalytic conversion of LDPE [9]. H-ZSM5 zeolite has yield mainly aromatics with carbons numbers less than 14 while zeolites such as H-mordenite and H-Theta-1 resulted in significant amount of jet-fuel range C<sub>11</sub>-C<sub>19</sub> [10]. Further study on a silicate-aluminate combination, silica-alumina and H-ZSM5 zeolite with a ratio of 9:1, was found to catalyze the pyrolysis of LDPE to yield 58.8 % gasoline fraction (C<sub>5</sub>-C<sub>12</sub>) and 26% aromatics [11]. HY and H-ZSM5 was found to have oil product with less yield while more aromatic characteristic at a higher reaction temperature [12]. HY was found in one report to have a slightly less conversion of 89.5 wt% then H-ZSM5 98.0 wt%, respectively [13]. The reactant to H-ZSM5 ratio of 2.0 was optimized to maximize the upgraded oil at 450 °C using microwave to provide heat [14]. Other than aluminosilicates, lead sulfide was able to catalyze the plastic to

paraffins and olefins, which have a total yield of 70% including hydrocarbons with a boiling point less than 350 °C [15]. Transition metals such as Pt and Rh supported by alumina were reported to complete the LDPE cracking at 425 °C in 1 hour, resulting in an increased saturated hydrocarbon up to 90 wt. % [16]. Catalysts with low cost have been reported as well. Activated carbons were applied as catalysts for converting LDPE to jet fuel ranged chemicals and hydrogen-enriched gases [17]. Kaolin, a mineral clay, has been used to catalyze the cracking of LDPE and led to a 90-95% yield of hydrocarbons which were C<sub>6</sub>-C<sub>20</sub> [18].

In this work, we have studied the selective production of gasoline ranged chemicals from LDPE upcycling using two categories of commercially available zeolites (three HY zeolites and one H-ZSM5 zeolite), which were widely adopted in the Fluid Catalytic Cracking (FCC) process in oil refinery. It was generally understood that, the upcycling of LDPE molecules went through random scission reactions, cleaved into radical pieces, then recombined into hydrocarbons, hydrogen, and carbon products [19,20]. However, to the best of our knowledge, the reaction mechanism associated with the product selectivity over different categories of zeolites still requires further study [21,22]. Specifically, the hydrogen transfer reactions over different zeolites were hypothesized to be related to zeolite structures. The hydrogen transfer reactions were also proposed to be directly related to the selectivity of the products. To have a better understanding on selective production, we have studied the performances of both HY and H-ZSM5 zeolites in simulated and batch scale pyrolysis. In addition, the potential mechanism of exothermic hydrogen transfer reactions and the resulting heat compensation to the overall endothermic process was elucidated. The novelties of this work are: (1) revealing the upcycling process of low-density polyethylene from the standpoint of the heat transfer; (2) disclosing the potential mechanism behind the selective production of the gasoline ranged alkanes with methyl

sidechains; (3) reporting a scientific method to analyze the oil products by combining simulated pyrolysis data by ex-situ TG-FTIR and fixed-bed data by GC-MS.

## **2. Materials and Methods**

### **2.1. Materials**

LDPE was a commercial product purchased from Sigma Aldrich (St. Louis, MO). The polymer powders have an apparent density of 0.92 g/cm<sup>3</sup>. The mass average molar mass  $M_w$  is 4000, and the number of average molar mass  $M_n$  is 1700. Zeolites were purchased from Zeolyst International (Delfzijl, Netherlands), as shown in Table 1. The texture properties of the zeolites have been characterized with a Micromeritics ASAP 2020+ (Micromeritics, Norcross, GA, USA). HY-400, HY-720, and HY-760 had Silica/Alumina (S/A) ratios of 5.1, 30, and 60, respectively. Commercial ZSM5 had a S/A ratio of 30, which possessed an ammonium nominal cation form. All zeolite catalysts were calcinated in a muffle furnace for 5 hours at 550 °C before use. The ZSM5 lost ammonia and was transformed into a hydrogen cation form, H-ZSM5. H-ZSM5 and HY-720 shared the same S/A ratio. Since these two zeolites shared a similar S/A ratio, the catalytic products resulted from them could be compared.

Table 1. The details about the zeolites used for the catalytic pyrolysis of LDPE

Parameters	HY-400	HY-720	HY-760	H-ZSM5
Surface Area* (m <sup>2</sup> /g)	628.83	756.50	768.44	353.84
Pore Volume^ (cm <sup>3</sup> /g)	0.358	0.483	0.507	0.212
Pore Size# (nm)	2.28	2.57	2.64	2.39
Particle Size (nm)	9.54	7.93	7.81	16.96
Commercial Label	CBV400	CBV720	CBV760	CBV 3024E
S/A Ratio	5.1	30	60	30

\*Surface area is calculated by BET method.

^Pore volume is calculated by single point adsorption total pore volume of pores less than 40.31 nm width at  $p/p^{\circ}=0.95$ .

#Pore size is calculated by adsorption average pore diameter ( $4V/A$  by BET)

## 2.2. Online TG-FTIR analysis

The pyrolytic products from the TG analyzer (TGA 8000, PerkinElmer, Waltham, MA, USA) were analyzed by an online Fourier-transform infrared spectroscopy (FTIR, Spectrum 2, PerkinElmer, Waltham, MA, USA). The pyrolytic products from the TG furnace were transported by the gas flow through the gas line and passed on to the ex-situ IR detector. The flow entering the IR detector was 90 mL/min, which was 90% of the total TG flow. The background IR spectrum was collected after 1.5 hours purge of nitrogen, prior to the start of the temperature ramp of the simulated pyrolysis inside the TG furnace. The step was to ensure that the background collected was nitrogen only. The IR spectra of the pyrolytic products from TG furnace were collected every minute as the temperature of the furnace was raised from 50 to 550 °C. Totally, 50 spectra were collected for the dynamic temperature ramp. Among these 50

spectra, the spectrum with highest intensity of transmittance was selected to represent products from each zeolite for further comparison of their catalytic performances.

Since this work was aiming at the production of gasoline ranged chemicals, the gas-line temperature was set at 150 °C for all tests. The 150 °C is the cut-off boiling point for the targeted gasoline ranged hydrocarbons with a carbon number no more than 9 based on their boiling points (Boiling points listed in Table S1). The gas-line temperature of TG-FTIR was controlled by a temperature control unit (TL8000, PerkinElmer, Waltham, MA, USA). The purpose of pre-setting the cut-off temperature was to build a reservoir of hydrocarbons with an upper limit of the carbon numbers, which was a common practice in industrial distillation of crude oil to produce gasoline and kerosene. A straight chain alkane typically has the highest boiling points among its isomers. Products with one or more carbon triple bond were highly unlikely, which was not observed in the FTIR analysis of the on-stream gas in this work. The current work has collected the spectra of pyrolytic products with a transportation line temperature at 150 °C for all zeolites tested, specifically for studying the gasoline fraction of the pyrolytic products. We understood that the evaporation could still happen below the boiling point, but the number of volatiles of these higher hydrocarbons resulted from evaporation could be extremely low.

### **2.3. Simulated LDPE slow pyrolysis**

Simulated slow pyrolysis of LDPE was conducted in a thermogravimetric (TG) analyzer (TGA SDT650, TA Instrument, New Castle, DE, USA) to find out the peaks of thermal degradation processes for both catalytic and non-catalytic cracking, as shown in Figure 1. The purging gas for the sample was nitrogen. In a typical experimental run, the flow rate was set at 100 mL/min. The ramping rate of 10 °C/min was pre-selected to simulate all samples for slow pyrolysis. The well-mixed LDPE/Zeolite blend was held at 50 °C for 2 hours inside the TG

furnace under nitrogen to purge out air. Based on the experimental observation, the non-catalytic pyrolysis of LDPE typically had a full degradation around 500-510 °C. Thus, the highest pyrolytic temperature was selected as 550 °C to ensure it has presented the entire degradation process. Regarding the catalytic LDPE pyrolysis, a common temperature to achieve a total degradation was less than 500 °C, depending on the LDPE to catalysis mass ratios. Therefore, to make the results comparable, the pyrolytic temperature was set as 550 °C for the catalytic LDPE pyrolysis as well, although the catalytic pyrolysis could have a total degradation at a temperature much lower than 500 °C. We understood that there were differences, in terms of the heat and mass transfer, between a TG simulated pyrolysis and a real-case scenario pyrolysis in a fixed/fluidized bed reactor. However, it was a rapid method to evaluate the catalytic performance for locating the reaction parameters [9,23].

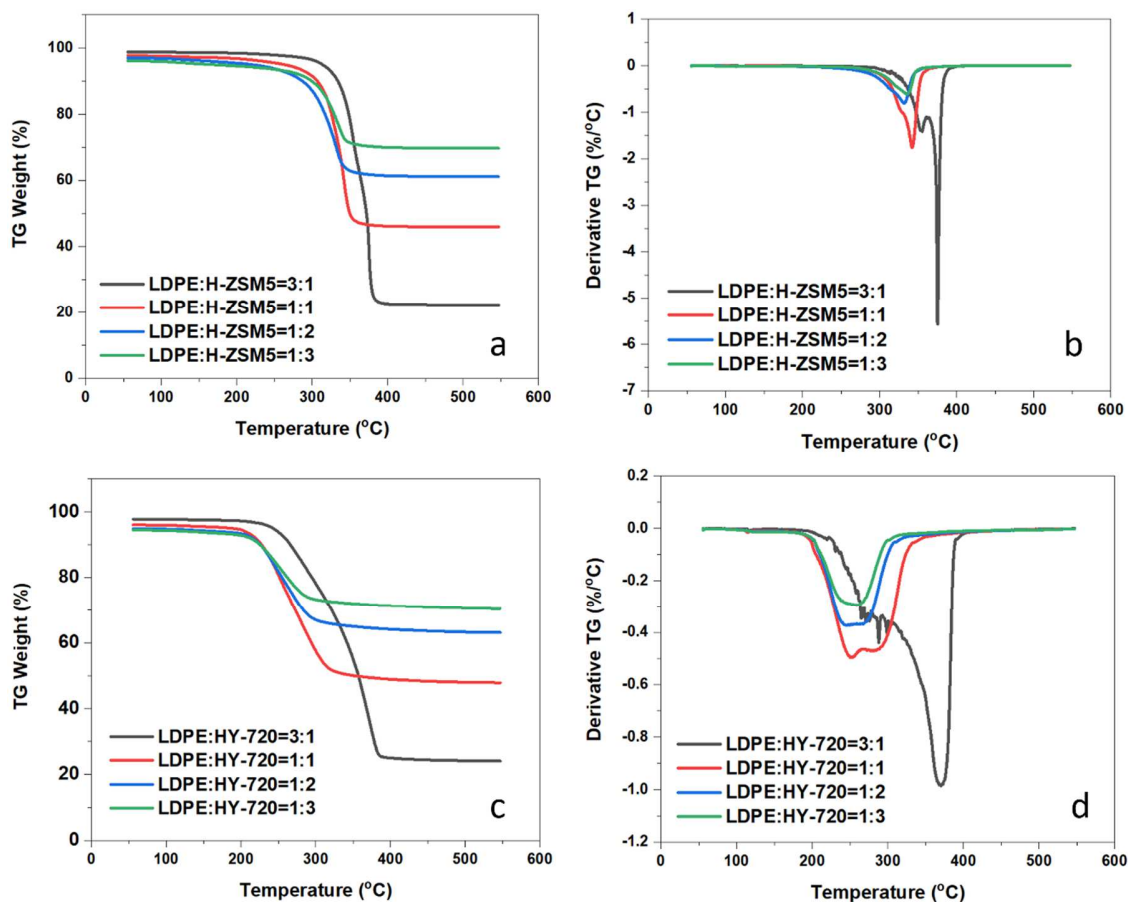


Figure 1. TGA of different mass ratios of LDPE to zeolites

### 2.3. Differential scanning calorimetry (DSC) analysis

The normalized heat flows of the simulated LDPE pyrolysis were measured using a simultaneous thermogravimetric-differential scanning calorimetry (TG-DSC) analyzer (TGA SDT650, TA Instrument, New Castle, DE, USA). The difference of normalized heat flow between the sample pan (with LDPE/Zeolite blend) and the empty control pan was recorded using the same ramping process as previously described in the section of simulated pyrolysis. Typically, a negative peak on the DSC curve indicated that the reaction was endothermic while a positive peak meant

exothermic. The results have shown that the thermogravimetric data from both TG analyzers were consistent.

## 2.4. Batch reaction and product analysis

Although the batch reaction was not the focus of the current work, a batch catalytic pyrolysis of LDPE in a fixed-bed reactor was carried to supplement the simulated catalytic LDPE pyrolysis, in terms of the product analysis. The batch catalytic pyrolysis of well mixed 6 g of LDPE/zeolite (1:1 mass ratio) was conducted with a ramping rate of 10 °C/min. Based on the results of simulated pyrolysis, the batch pyrolytic temperature was selected as 350 °C. Typically, a batch pyrolysis was completed within 30 min. The heat was kept for up to 1 hour to evaporate all the liquid products from the reactor. The liquid products from this batch reaction were condensed with cycling tap water. The condensed liquid products were analyzed by a gas chromatography-mass spectrometry (GC-MS). The details about this GC-MS have been listed in Table 2. For MS, the first 5 min was not analyzed because of solvent. The total analysis time for MS was 36 min.

Table 2. The properties of the GC-MS used in this work.

Item	Details
GC model	PerkinElmer Clarus 590
MS model	PerkinElmer Clarus SQ8T
GC column model	Restek Rtx®-1 column, 0.25mm(30m)
Column Temperature	200 °C
Column Ramping Rate	5 °C/min
Holding Time	26 min

## 3. Results and discussion

### 3.1. Zeolites and product functional groups

To study the effect of zeolites on the product selectivity, the pyrolytic product functional groups were analyzed by the online TG-FTIR. The spectrum with the highest transmittance was selected to represent each zeolite (As shown in Figure 2). The resulted FTIR spectra with a primary alkane characteristic from non-catalytic LDPE pyrolysis from this work was consistent with literature reports [24,25]. Products analysis of a pure LDPE pyrolysis from a fixed bed reactor showed that n-paraffins amount was more than 3 times of 1-olefins [26]. LDPE catalytic pyrolysis products were mainly alkanes over HY zeolites while unsaturated alkenes or aromatics over H-ZSM5 in the current work. The details of the product IR spectra analysis were listed in Figure 2. The assignment of peaks by functional groups was listed in Table S2-4, based on a previous literature [27].

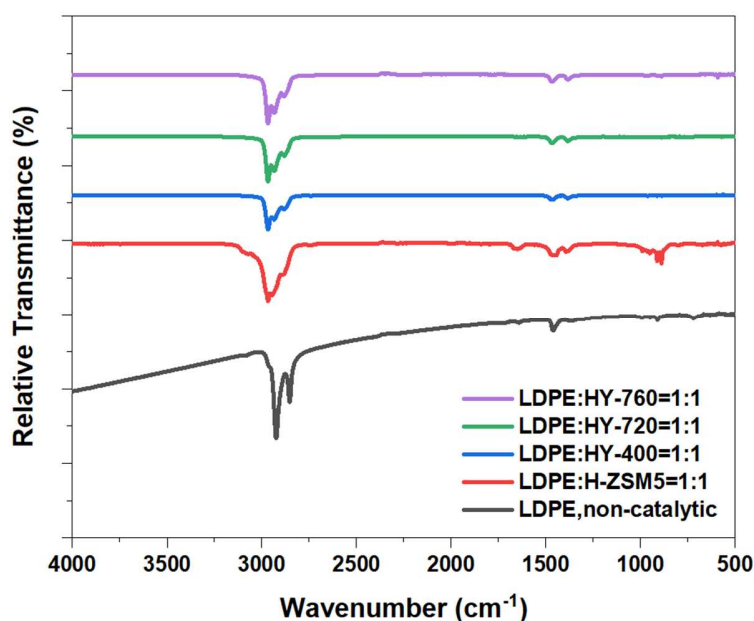


Figure 2. Functional groups survey by online-FITR for all tested zeolites

The non-catalytic pyrolysis of LDPE has yielded mainly alkanes with a high methylene/methyl ratio, as shown in Figure 3. The assignment of product peaks was listed in

Table S2. Although a weak peak around  $3080\text{ cm}^{-1}$  indicated a small number of alkenes or aromatics, the spectra have shown mainly C-H stretching band of alkanes at  $2800\text{-}3000\text{ cm}^{-1}$ , further confirmed by C-H bending peak of alkanes around  $1450$  and  $1465\text{ cm}^{-1}$ . The result has shown that the pyrolysis of LDPE produced primarily alkanes with a small number of unsaturated hydrocarbons. Thus, the alkane products detected by the IR spectrum were mainly hydrocarbons with chain length of  $\text{C}_9$  or less. The highest intensity of gas phase products being flowed through the FTIR detector occurred when the sample in the TG furnace was at  $500\text{ }^\circ\text{C}$ . The spectrum at this pyrolytic temperature was selected to represent the non-catalytic pyrolysis of pure LDPE.



Figure 3. Detailed functional groups comparison: (a) and (b), between H-ZSM5 and HY-720; (c) and (d) among HY zeolites.

Products from LDPE pyrolysis catalyzed by H-ZSM5 had a substantial amount of carbon double bonds, which was revealed by presenting peaks at 3100-3000  $\text{cm}^{-1}$ . The pyrolytic products from LDPE catalyzed by H-ZSM5 was analyzed and shown in Figure 3a (C-H stretching region) and 2b (Fingerprint region). The interpretation of IR peaks was listed in Table S3. The results showed that the products consisted of alkenes, aromatics, and alkanes. The relative intensity of alkenes or aromatics, in a qualitative manner, was higher than the ones from pyrolysis of pristine LDPE. The highest intensity of the gas phase occurred when the sample in the TG furnace was at 350  $^{\circ}\text{C}$ , which was selected to be a representative spectrum for H-ZSM5.

The products from catalytic pyrolysis of LDPE with HY-400, HY-720, HY-760 were examined and shown in Figure 3c (C-H stretching region) and 3d (Fingerprint region). The spectrum with the highest intensity of transmittance can be located around 310  $^{\circ}\text{C}$  for all three HY zeolites. The assignment of peaks found in the selected spectrum was listed in Table S4. Catalytic pyrolysis of LDPE with HY zeolites has yielded products with a lower methylene/methyl ratio than that of pure LDPE. The spectra showed a sharp peak around 2967  $\text{cm}^{-1}$ , while spectra of pure LDPE displayed only a medium climbing shoulder around the same wavenumber. It indicated that the products of HY zeolites catalytic pyrolysis consisted of hydrocarbons either with shorter carbon chains or more side chains than non-catalytic products of LDPE pyrolysis. It appeared that the catalyst has helped further breaking the oligomers, which can be referred as the secondary cracking. Based on the five clear symbolic alkane peaks, the products obtained from using HY zeolites were characterized as mainly saturated hydrocarbons. Peaks at 2966, 2934 and 2881  $\text{cm}^{-1}$  referred to C-H stretching of alkanes. Peak at 1465  $\text{cm}^{-1}$  referred to alkane C-H bending. The peak at 1385  $\text{cm}^{-1}$  referred to gem dimethyl, indicating there

were side-chain methyl groups. Since few C=C peaks were observed, the products did not have a detectable number of aromatics or alkenes.

Different Silica/Alumina ratios of zeolites were tested and compared in Figure 3c and 3d. Catalytic products from different S/A ratios showed no significant difference among the spectrum patterns, both in the C-H stretching and the fingerprint regions. The spectra of the pyrolytic products of HY zeolites were very similar to the IR spectrum of hexane, 3-methyl- found in the NIST library [28]. However, it must be stressed that the products should have a mixture of different hydrocarbons rather than a pure compound. The height ratios of peak 2967 to 2934  $\text{cm}^{-1}$  were 1.40, 1.31 and 1.28 for S/A ratio of 5.1, 30 and 60, indicating that heavier hydrocarbons were obtained when the S/A ratios were increased. Since the spectra showed significant alkane peaks, the IR spectra of HY zeolites can generally be interpreted by matching the spectra with a standard IR spectrum of a known alkane. The IR spectrum of n-hexane had a similar transmittance height at 2967 and 2934  $\text{cm}^{-1}$  due to a methylene/methyl molar ratio of 2 [29]. When the methylene/methyl molar ratio is over 2, the peak height at 2967  $\text{cm}^{-1}$  of n-alkane was lower than 2934  $\text{cm}^{-1}$ , and vice versa but with a few exceptions for light hydrocarbons [29]. Thus, after matching the spectra to the NIST library [28], the major products from HY zeolites should be C<sub>6</sub>-C<sub>9</sub> (gas-line temperature was set at 150 °C). Based on IR spectra from catalytic products of HY zeolites, the intensity of methyl was higher than methylene, indicating that the overall molar ratio of methylene/methyl was less than 2. Further examination of the IR fingerprint region (500-1500  $\text{cm}^{-1}$ ) confirmed that light hydrocarbons (C<sub>1</sub>-C<sub>4</sub>) were not present in a significant amount.

Therefore, different HY zeolites did not show a significant difference in product functional groups. Further study has been focused on the detailed comparisons between HY-720

and H-ZSM5. While belonging to different zeolite categories, these two zeolites have the same silica/alumina ratio. Thus, their catalytic performance could be compared.

### 3.2. Zeolite mass ratios and LDPE catalytic pyrolysis

HY-720 and H-ZSM5 were selected for comparison since they shared the same silica/alumina ratio. The TGA results of catalytic LDPE pyrolysis have been displayed in Figure 1a and 1c. The derivative thermogravimetric (DTG) was also given in Figure 1b and 1d. In general, the results have shown that the weight loss of LDPE took place at a lower temperature when a higher zeolite mass ratio was adopted, despite of zeolite category. It indicated that the zeolites have reduced the energy required to crack the LDPE macromolecule, resulting in a lower temperature requirement. The exact degradation peaks have been listed in Table 3 for detailed comparison between two types of catalysts. It has shown that the HY-720 with 50% mass ratio resulted in two pyrolytic DTG peaks at 252 and 281 °C. The H-ZSM5 with the same mass ratio had two pyrolytic peaks at 329 and 342 °C.

Table 3. The effect of catalyst ratios on the pyrolytic weigh loss peak of LDPE

	Mass Ratio	Pyrolytic 1 <sup>st</sup> Peak (°C)	Pyrolytic 2 <sup>nd</sup> Peak (°C)
LDPE: HY-720	3:1	288	370
	1:1	252	281
	1:2	246	266
	1:3	243	259
LDPE:H-ZSM5	3:1	354	375
	1:1	328	342
	1:2	317	332
	1:3	324	337

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Pure LDPE	-	462	477
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### 3.3. Zeolite type and endothermic reactions

The DSC results from the catalytic LDPE pyrolysis using HY-720 and H-ZSM5 were shown in Figure 4. A negative endothermic peak at 114 °C was observed for all samples, due to the melting of LDPE. The temperature of this phase-changing peak was not affected by the catalyst mass ratio. The negative peaks observed above 200 °C were led by the endothermic pyrolytic cracking of LDPE. Theoretically, the pyrolytic peak position of DSC should be consistent with the DTG (in Figure 1) while the phase changing peaks of DSC should not appear on DTG, since the phase changing process from solid to liquid did not have weight loss associated with it.

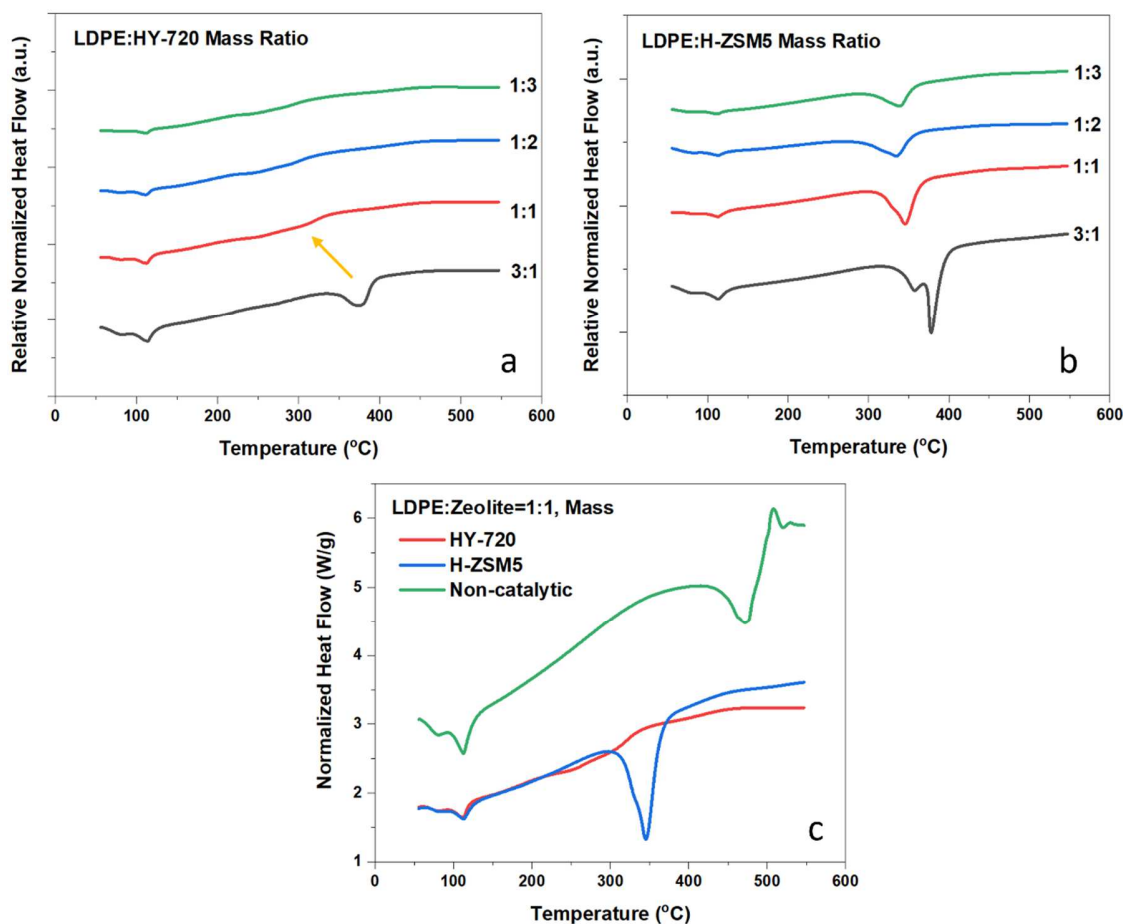


Figure 4. Differential scanning calorimetry results of HY-720 and H-ZSM5.

It showed that the HY-720 have a lower activation energy for fully cracking the LDPE. The intensity of the endothermic peak from the LDPE pyrolysis with HY-720 decreased to an invisible level when the catalyst mass ratio was increased from 25.0 % to 75.0 %. The catalytic pyrolysis of LDPE using H-ZSM5 had a decreased relative normalized heat flow of endothermic peak when the mass ratio was increased from 25.0 % to 66.7 %. However, when the catalyst mass ratio of H-ZSM5 was increased further to 75.0 %, the relative normalized heat flow has not been increased. When it came to the absolute normalized heat flow as shown in Figure 4c, the H-ZSM5 displayed a significant endothermic peak while the HY-720 did not.

The observation could be simply explained as the less LDPE mass percentage when more zeolite catalyst was added into the blend, which applied to both types of catalysts. Essentially, both HY and H-ZSM5 had a decreased intensity for the pyrolytic peaks in general. However, the negative peaks eventually became low enough and invisible in HY zeolites. It was speculated that there were certain exothermic reactions from which heat released compensates the endothermic cracking of LDPE. It was believed that the primary reaction of LDPE degradation was the endothermic random chain scissoring, forming fractionated oligomers. The secondary reactions of LDPE degradation were the cracking of these oligomers. In general, a combination of free radical mechanism and carbenium ion mechanism were proposed for thermo-catalytic cracking of polymers [30]. One literature regarding the catalytic cracking of LDPE using zeolite was supporting the proposed mechanism combination as well [31]. Thus, it was reasonable to believe that the effect might be related to the secondary reactions. These phenomena could be caused by the presence of side reactions that influence heat balance in the system. The possible heat compensation could come from certain exothermic reactions, leading to a lower overall energy consumption.

### **3.4. Catalyst type and gasoline ranged products**

Catalytic LDPE pyrolysis have presented a similar product composition using three HY zeolites. To better understand product distribution, HY-720 was selected as a representative HY zeolite for a test in a fixed bed reactor with catalyst mass ratio being 50%. The results of GC-MS for both HY-720 and H-ZSM5 could be found in Figure 5 regarding the carbon number distribution of the products and the most possible chemical formula predicted by a built-in NIST

library within the GC-MS software. The product analysis stressed on the gasoline ranged products.

The result showed that most of the H-ZSM5 catalytic products were unsaturated. In addition, the products consisted of a significant number of aromatics. On the other hand, it was clear that the HY-720 catalytic products had the highest intensity for C<sub>7</sub> (hexane, 3-methyl and hexane, 2-methyl), since both have the highest relative intensities than others (C<sub>8</sub>, C<sub>9</sub>, C<sub>10</sub> and heavier hydrocarbons). The results showed that the products were mainly C<sub>7</sub>-C<sub>10</sub> alkanes with very limited number of aromatics. The highest intensity had showed up for C<sub>7</sub> alkane. The result of GC-MS was highly consistent with the products revealed by the IR spectra. The IR spectra from the HY zeolites were extremely similar to the IR spectra of hexane, 3-methyl- from the NIST library [28].

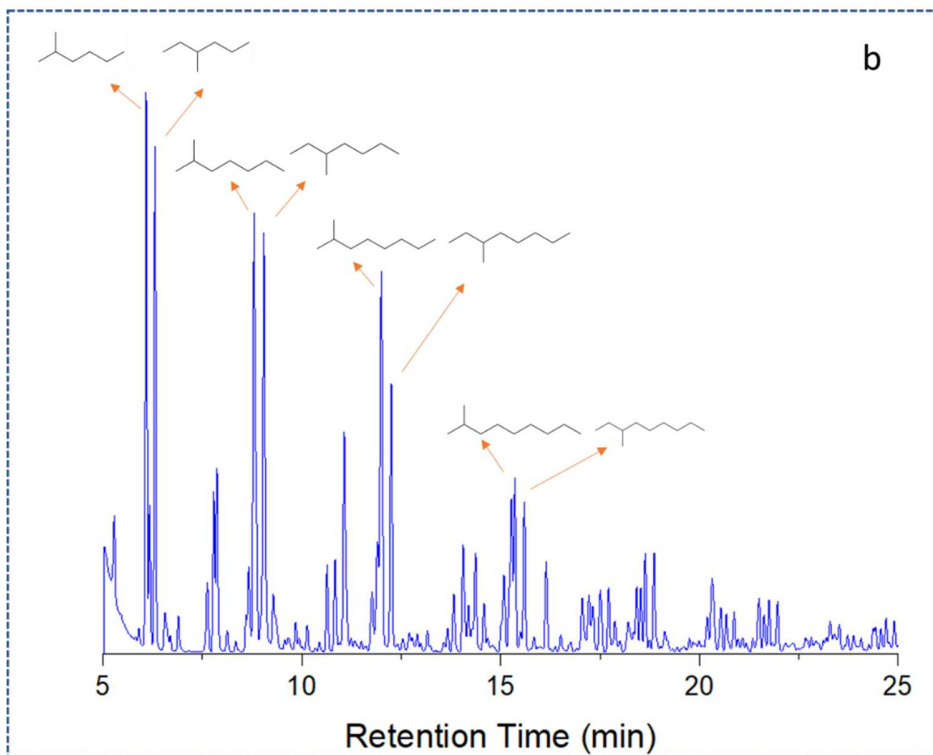
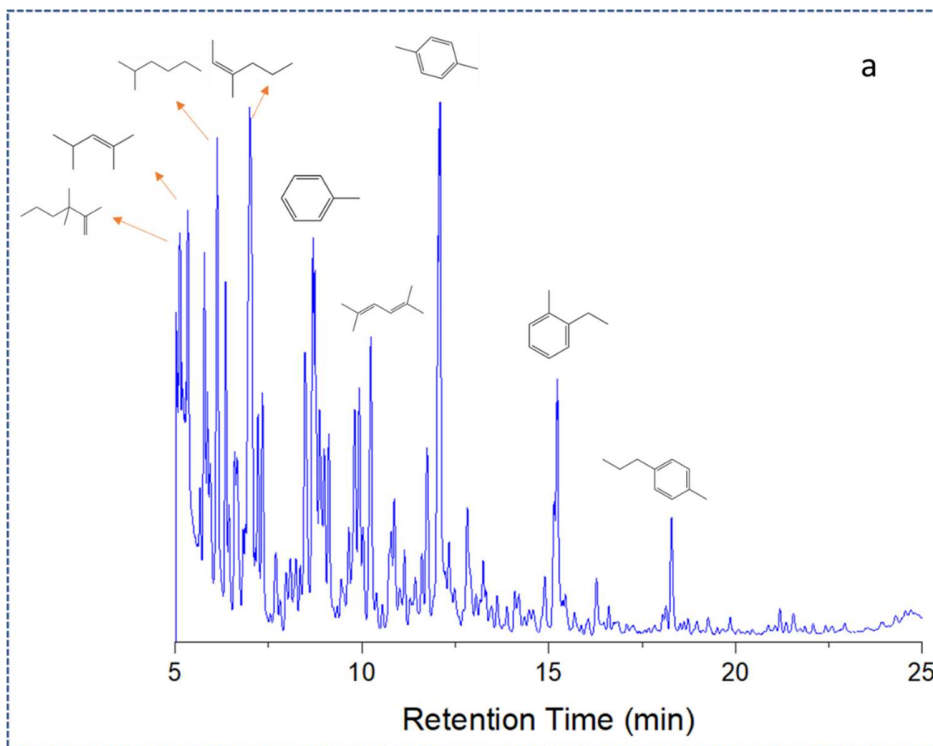


Figure 5. The liquid product distribution of: (a) LDPE to H-ZSM5 mass ratio at 1:1; (b) LDPE to HY-720 mass ratio at 1:1.

Zeolite structures played a key role in the product selectivity. Previously, Figure 3 has showed the spectra of pyrolytic products from HY-720 and H-ZSM5. Both zeolites had the same S/A ratio and catalyst/LDPE ratio. Generally, non-catalytic products from LDPE pyrolysis showed mainly long chain alkanes with a minority of alkenes. HY zeolites, regardless of difference in S/A ratios, generally yielded many alkanes. The difference of the products could be differentiated from the C-H stretching around  $3000\text{ cm}^{-1}$  and C=C stretching/bending information within  $500\text{-}1500\text{ cm}^{-1}$ . H-ZSM5 was showing a visible number of unsaturated products, such as alkenes or aromatics.

Further analysis showed that HY zeolites has yielded mainly alkanes, which was proved by C-H stretching peaks at  $2966$ ,  $2934$ , and  $2881\text{ cm}^{-1}$ . The alkyl products had a low methylene/methyl ratio, which was indicated by the higher intensity of transmittance peak around  $2966\text{ cm}^{-1}$  (assigned to  $-\text{CH}_3$ ) than peaks at  $2934$  and  $2881\text{ cm}^{-1}$  (assigned to  $-\text{CH}_2-$ ). In additions, the medium intensity peaks at  $1466$  and  $1384\text{ cm}^{-1}$  signaled the bending of C-H in methylene and gem dimethyl, indicating that the alkane products had side-chain methyl group, which was highly desirable for gasoline range fuels. To produce gasoline-range chemicals, the content of side chain and cyclic hydrocarbon should be high, since these two were beneficial for promoting the octane number and complete burning, while the content of straight chain and aromatics should be low [32,33]. Large peaks of alkenes/aromatics were not observed with the catalytic pyrolysis of LDPE using HY zeolites. No significant peaks of alkenyl C-H or C=C was shown on the IR spectrum of the gaseous product, which was further confirmed by GC-MS analysis of the HY catalytic products. In contrast, H-ZSM5 has yielded alkanes and alkenes/aromatics. The IR spectra show a visible alkene functional groups such as a shoulder

around 3100-3000  $\text{cm}^{-1}$ , indicating alkenyl C-H stretching, and a peak at 1651  $\text{cm}^{-1}$ , signaling C=C stretching. The combination of 888 and 1651  $\text{cm}^{-1}$  indicated the presence of vinylidene groups (-CH=CH<sub>2</sub>).

Industrially, Y zeolite was widely used in fluid catalytic cracking (FCC) to transform crude oil into gasoline [34]. The crude oil consisted of heavy hydrocarbons with molecule weights from 200 to 600. The cracking of LDPE could be a similar process. When LDPE was heated above 110 °C, it melted into a hydrocarbon fluid. The Y zeolite is made of 12-membered-ring cages, having diameters ~1.3 nm, and connecting windows between cages have diameters ~0.74 nm. ZSM-5 was commonly used industrially for isomerization of xylene, specifically meta-xylene to para-xylene, or trans-alkylation reactions. ZSM-5 consists of penta-ring units, which have intersecting proportional straight and sinusoidal ten-membered-ring pores, the diameter of which are between 0.50 and 0.56 nm. HY is generally to be considered more spacious than ZSM-5. Both zeolites have worked through the active acidic sites, which are usually reported as Bronsted acid rather than Lewis acid, or Lewis acid assisting the primary Bronsted acid in some cases. Aluminum content determines the acidic extent of zeolites. The HY is a strong acidic zeolite. It was reported that H-ZSM5 catalyst could increase the aromatic content of pyrolytic products from LDPE pyrolysis [10]. It is highly related to the shape selectivity of the zeolite. The H-ZSM5 has a better shape selectivity, ion exchange capability as well as 3-D crystal structure which could help yield more aromatics [35]. In addition, the reference pointed out no higher hydrocarbon was detected than C<sub>14</sub>. It was worth noting that the PE/zeolite mass ratio in this report was 5:1. The reactor was placed into a furnace that was already set at 350 °C. The residence time was 2 hours. The results from this referred work

showed a 49% conversion of LDPE to gaseous/volatile products while 46% conversion to a soft solid that could be melted at 65 °C (wax alike).

The difference in product distribution between pyrolysis of LDPE using HY zeolite and H-ZSM5 was reported previously. With separate beds for LDPE and zeolite, the yield of pyrolytic oil was 88% over H-ZSM5 (S/A Ratio 50), and 86% over HY zeolite (S/A Ratio 11), which were higher than that of non-catalytic pyrolysis [12]. Furthermore, the report has pointed out that the gas yield was relatively low. Less than 5% of C<sub>1</sub>-C<sub>4</sub> gases was obtained. This could explain why the unsaturated C<sub>2</sub>-C<sub>4</sub> in the current work did not affect the IR spectra, largely due to the low overall concentrations. The non-condensed gas composition shifted from propane and iso-butane dominated alkanes to propane and methane dominated alkanes over HY zeolite when pyrolytic temperature was increased from 400 to 600 °C [12]. It should be noted that there were two differences between the reported and the current work. The reported work adopted separate bed for LDPE and zeolite while the current work used a mixture bed reactor. Another difference was the ramping rate of pyrolytic temperature. In the reported work, the feed was directly added into a furnace over 400 °C. In the current study, the mixed feed and catalyst were heated gradually from 50 to 550 °C with a ramping rate of 10 °C/min. Their study revealed that H-ZSM5 was producing more gas than HY at one pyrolytic temperature. However, further testing should be conducted to draw the conclusion since the zeolites they have used had substantially different S/A ratios, which led to significantly different acidities. It was widely acknowledged that the carbon numbers have shifted from high to low when catalysts were added into the LDPE [36]. Different from Bagri's report, the current work did not find an increased aromatic content when it came to HY, but we did notice a rise in the case of H-ZSM5. It was reported that the

products of isobutane and isopentane were generated at a low temperature pyrolysis of polyethylene, which were due to the further scission of C<sub>9</sub> chain [20].

### 3.5. Possible mechanism of heat compensation effect

A significant heat compensation effect was observed when HY-720 was used as catalysts for catalytic pyrolysis of LDPE. When the catalyst mass ratio of LDPE/zeolite was over 50%, the DSC analysis showed that the catalytic pyrolysis of LDPE using H-ZSM5 had an apparent negative pyrolytic peak while the HY-720 did not show. It was speculated that there were certain exothermic reactions which could compensate the overall endothermic heat requirement. The possible pathways for the heat compensation effect were shown in Figure 6.

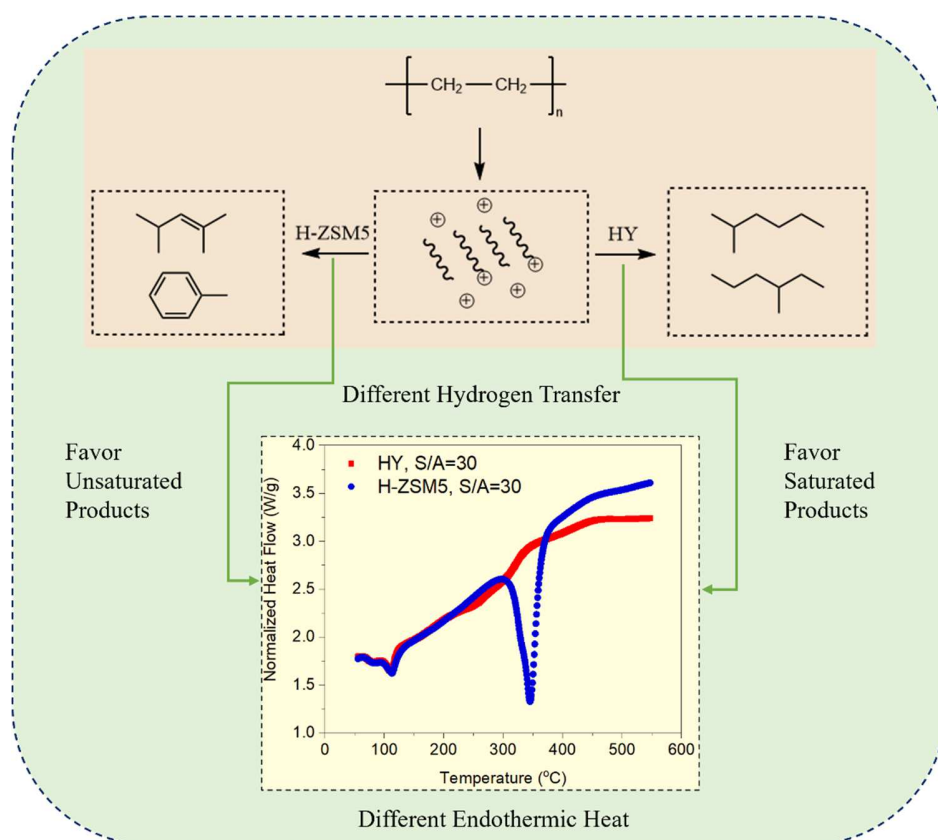


Figure 6. Possible pathways for the heat compensation effect

The products analysis from TG-FTIR and GC-MS for HY-720 have clearly shown saturated products. Thus, hydrogen radicals release from the cracking was subsequently consumed to form more saturated hydrocarbons. However, the overall hydrogen to carbon atomic ratio was only 2. It meant that more coke will be formed when HY-720 was used as a catalyst. This was consistent with the experimental observation that more coke was formed using HY-720 than H-ZSM5 at mass ratio 1:1. During the pyrolysis, the color of HY-720 changed from white to dark while H-ZSM5 remained white. The transformation of color could be interpreted as coke formation which was commonly observed in HY-720 while it was not often in H-ZSM5. It was reported in the literature for the comparison of coke formation during the polyethylene pyrolysis using HY zeolites and H-ZSM5. The report has shown that the coke produced by H-ZSM5 was about 0.05 g/g-catalyst while HY zeolite generated about 0.2 g/g-catalyst [37]. This was due to the larger porous structure that HY zeolite had, making it more easily to deactivate by coke disposition. The pyrolytic oil can penetrate the HY zeolites pores and be reformed [8]. We anticipate that, in an industrial reactor design, catalytic pyrolysis of plastics would be operated in a fluid catalytic cracking (FCC) reactor that is similar to those used in petroleum refinery. In the FCC reactor system, catalyst regeneration is carried out through oxidation of coke deposit during which heat is recovered to supply endothermic pyrolysis reaction.

The HY zeolite was able to catalyze the hydrogen transfer reactions of unsaturated hydrocarbons. GC-MS showed that HY had a negligible number of aromatics. DSC of the catalytic pyrolysis of the LDPE using HY zeolites showed endothermic pyrolytic peaks with way less intensity than non-catalytic pyrolysis, almost invisible endothermic peaks. It means that it is reasonable to believe that some exothermic reactions must take place to compensate the endothermic heat. It

was reported that the zeolite can also serve as a hydrogen transfer catalyst [38]. Both HY and H-ZSM5 could catalyze the hydrogen transfer to form iso-alkenes and aromatics in the beginning stage. HY could further catalyze the dehydrogenation of aromatics to form multi-ring polyaromatics [39]. The hydrogen radicals of these aromatics were transferred to the iso-alkenes to form iso-alkanes in the second stage, which is exothermic. The H-ZSM5 was less likely to catalyze the reactions in the second stage. Thus, less exothermic reactions were taking place [8,40].

#### **4. Conclusion**

This study demonstrated how polyethylene can be a viable feedstock for the generation of molecular hydrocarbon products. The selection of zeolites has become important in determining the product compositions. TGA-FTIR online analysis of the functional groups has revealed that the product composition has shifted from alkanes to unsaturated alkenes and aromatics when the catalyst was changed from HY zeolite to H-ZSM5. For HY zeolite, exothermic hydrogen transfer reactions compensated the heat required by endothermic pyrolytic reaction, which was evidenced by the significantly weakened endothermic peak on DSC curve of LDPE catalytic pyrolysis. This effect has occurred when the catalyst mass ratio passed 50%, indicating that the excessive HY helped form saturated products. The hydrogen transfer reactions released heat offsetting endothermic pyrolytic reaction and resulting in a reduced overall endothermic heat requirement. The offsetting was not observed in H-ZSM5 catalytic process. HY zeolites could be adopted for selectively producing alkanes while H-ZSM5 for aromatics. In addition, HY zeolites could be thermodynamically favor since it could potentially reduce the overall energy consumption. The limitation of this work is to clearly measure the energy consumption and present the exact

concentrations of each product in a quantitatively manner. The authors expected to conduct these tasks in the near future. Clearly, further improvement of heat balance and product control of this approach are needed for any large-scale practical utilization.

### **Author contribution**

Changle Jiang: conceptualization, methodology, investigation, data curation, formal analysis, writing-original draft, writing-review & editing. Yuxin Wang: methodology, investigation. Thang Luong: investigation. Brandon Robinson: investigation, data curation. Wei Liu: methodology, funding acquisition. Jianli Hu: conceptualization, methodology, writing-review & editing, supervision, funding acquisition.

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### **References**

- [1] R. Basuhi, E. Moore, J. Gregory, R. Kirchain, A. Gesing, E.A. Olivetti, Environmental and economic implications of U.S. postconsumer plastic waste management, *Resour. Conserv. Recycl.* 167 (2021) 105391.  
<https://doi.org/https://doi.org/10.1016/j.resconrec.2020.105391>.

- [2] J. Jambeck, R. Geyer, C. Wilcox, T.R. Siegler, M. Perryman, A. Andrady, R. Narayan, K.L. Law, the Ocean : the Ocean :, *Mar. Pollut.* 347 (2015) 768-.  
<https://science.sciencemag.org/CONTENT/347/6223/768.abstract>.
- [3] C.M. Rochman, A. Tahir, S.L. Williams, D. V Baxa, R. Lam, J.T. Miller, F.-C. Teh, S. Werorilangi, S.J. Teh, Anthropogenic debris in seafood: Plastic debris and fibers from textiles in fish and bivalves sold for human consumption, *Sci. Rep.* 5 (2015) 14340.  
<https://doi.org/10.1038/srep14340>.
- [4] S.B. Borrelle, C.M. Rochman, M. Liboiron, A.L. Bond, A. Lusher, H. Bradshaw, J.F. Provencher, Why we need an international agreement on marine plastic pollution, *Proc. Natl. Acad. Sci. U. S. A.* 114 (2017) 9994–9997.  
<https://doi.org/10.1073/pnas.1714450114>.
- [5] J. Hopewell, R. Dvorak, E. Kosior, Plastics recycling: Challenges and opportunities, *Philos. Trans. R. Soc. B Biol. Sci.* 364 (2009) 2115–2126.  
<https://doi.org/10.1098/rstb.2008.0311>.
- [6] J.M. Garcia, M.L. Robertson, The future of plastics recycling, *Science* (80-. ). 358 (2017) 870–872. <https://doi.org/10.1126/science.aag0324>.
- [7] J.M. García, Catalyst: Design Challenges for the Future of Plastics Recycling, *Chem.* 1 (2016) 813–815. <https://doi.org/10.1016/j.chempr.2016.11.003>.
- [8] A.R. Songip, T. Masuda, H. Kuwahara, K. Hashimoto, Test to screen catalysts for reforming heavy oil from waste plastics, *Appl. Catal. B, Environ.* 2 (1993) 153–164.  
[https://doi.org/10.1016/0926-3373\(93\)80045-F](https://doi.org/10.1016/0926-3373(93)80045-F).

- [9] P.L. Beltrame, P. Carniti, G. Audisio, F. Bertini, Catalytic degradation of polymers: Part II-Degradation of polyethylene, *Polym. Degrad. Stab.* 26 (1989) 209–220.  
[https://doi.org/10.1016/0141-3910\(89\)90074-8](https://doi.org/10.1016/0141-3910(89)90074-8).
- [10] R.C. Mordi, J. Dwyer, R. Fields, H-ZSM-5 catalysed degradation of low density polyethylene, polypropylene, polyisobutylene and squalane: Influence of polymer structure on aromatic product distribution, *Polym. Degrad. Stab.* 46 (1994) 57–62.  
[https://doi.org/10.1016/0141-3910\(94\)90109-0](https://doi.org/10.1016/0141-3910(94)90109-0).
- [11] Y. Uemichi, J. Nakamura, T. Itoh, M. Sugioka, A.A. Garforth, J. Dwyer, Conversion of polyethylene into gasoline-range fuels by two-stage catalytic degradation using silica-alumina and HZSM-5 zeolite, *Ind. Eng. Chem. Res.* 38 (1999) 385–390.  
<https://doi.org/10.1021/ie980341+>.
- [12] R. Bagri, P.T. Williams, Catalytic pyrolysis of polyethylene, *J. Anal. Appl. Pyrolysis.* 63 (2002) 29–41. [https://doi.org/10.1016/S0165-2370\(01\)00139-5](https://doi.org/10.1016/S0165-2370(01)00139-5).
- [13] A. Marcilla, M.I. Beltrán, R. Navarro, Thermal and catalytic pyrolysis of polyethylene over HZSM5 and HUSY zeolites in a batch reactor under dynamic conditions, *Appl. Catal. B Environ.* 86 (2009) 78–86. <https://doi.org/10.1016/j.apcatb.2008.07.026>.
- [14] X. Zhang, H. Lei, G. Yadavalli, L. Zhu, Y. Wei, Y. Liu, Gasoline-range hydrocarbons produced from microwave-induced pyrolysis of low-density polyethylene over ZSM-5, *Fuel.* 144 (2015) 33–42. <https://doi.org/10.1016/j.fuel.2014.12.013>.
- [15] J. Shah, M.R. Jan, Z. Hussain, Catalytic pyrolysis of low-density polyethylene with lead sulfide into fuel oil, *Polym. Degrad. Stab.* 87 (2005) 329–333.

<https://doi.org/10.1016/j.polymdegradstab.2004.08.016>.

- [16] N. Insura, J.A. Onwudili, P.T. Williams, Catalytic pyrolysis of low-density polyethylene over alumina-supported noble metal catalysts, *Energy and Fuels*. 24 (2010) 4231–4240. <https://doi.org/10.1021/ef100227f>.
- [17] Y. Zhang, D. Duan, H. Lei, E. Villota, R. Ruan, Jet fuel production from waste plastics via catalytic pyrolysis with activated carbons, *Appl. Energy*. 251 (2019) 113337. <https://doi.org/10.1016/j.apenergy.2019.113337>.
- [18] W. Luo, Z. Fan, J. Wan, Q. Hu, H. Dong, X. Zhang, Z. Zhou, Study on the reusability of kaolin as catalysts for catalytic pyrolysis of low-density polyethylene, *Fuel*. 302 (2021) 121164. <https://doi.org/10.1016/j.fuel.2021.121164>.
- [19] R.C. Mordi, R. Fields, J. Dwyer, Thermolysis of low density polyethylene catalysed by zeolites, *J. Anal. Appl. Pyrolysis*. 29 (1994) 45–55. [https://doi.org/10.1016/0165-2370\(93\)00789-P](https://doi.org/10.1016/0165-2370(93)00789-P).
- [20] Y. Ishihara, H. Nanbu, K. Saido, T. Ikemura, T. Takesue, Back Biting Reactions during the Catalytic Decomposition of Polyethylene, *Bull. Chem. Soc. Jpn.* 64 (1991) 3585–3592. <https://doi.org/10.1246/bcsj.64.3585>.
- [21] D.W. Park, E.Y. Hwang, J.R. Kim, J.K. Choi, Y.A. Kim, H.C. Woo, Catalytic degradation of polyethylene over solid acid catalysts, *Polym. Degrad. Stab.* 65 (1999) 193–198. [https://doi.org/10.1016/S0141-3910\(99\)00004-X](https://doi.org/10.1016/S0141-3910(99)00004-X).
- [22] N.D. Hesse, R. Lin, E. Bonnet, I.I.I. Jesse Cooper, R.L. White, In situ analysis of volatiles obtained from the catalytic cracking of polyethylene, *J. Appl. Polym. Sci.* 82 (2001)

- 3118–3125. <https://doi.org/10.1002/app.2168>.
- [23] J.W. Park, S.C. Oh, H.P. Lee, H.T. Kim, K.O. Yoo, A kinetic analysis of thermal degradation of polymers using a dynamic method, *Polym. Degrad. Stab.* 67 (2000) 535–540.
- [24] A.Y. Waziri, A.A. Osigbesan, F.N. Dabai, S.M. Shuwa, A.Y. Atta, B.Y. Jibril, Catalytic reforming of gaseous products from pyrolysis of low-density polyethylene over iron-modified ZSM-5 catalysts, *Appl. Petrochemical Res.* 9 (2019) 101–112. <https://doi.org/10.1007/s13203-019-0230-4>.
- [25] A.K. Panda, A. Alotaibi, I. V. Kozhevnikov, N.R. Shiju, Pyrolysis of Plastics to Liquid Fuel Using Sulphated Zirconium Hydroxide Catalyst, *Waste and Biomass Valorization.* 11 (2020) 6337–6345. <https://doi.org/10.1007/s12649-019-00841-4>.
- [26] L. Ballice, M. Yüksel, M. Sağlam, R. Reimert, H. Schulz, Classification of volatile products from the temperature-programmed pyrolysis of low- and high-density polyethylene, *Energy and Fuels.* 12 (1998) 925–928. <https://doi.org/10.1021/ef980004d>.
- [27] M.R. Jung, F.D. Horgen, S. V. Orski, V. Rodriguez C., K.L. Beers, G.H. Balazs, T.T. Jones, T.M. Work, K.C. Brignac, S.J. Royer, K.D. Hyrenbach, B.A. Jensen, J.M. Lynch, Validation of ATR FT-IR to identify polymers of plastic marine debris, including those ingested by marine organisms, *Mar. Pollut. Bull.* 127 (2018) 704–716. <https://doi.org/10.1016/j.marpolbul.2017.12.061>.
- [28] W.E. Wallace, “Infrared Spectra”, in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P.J. Linstrom and W.G. Mallard, National Institute

- of Standards and Technology, Gaithersburg MD, 20899, n.d.  
<https://doi.org/https://doi.org/10.18434/T4D303>.
- [29] B.C. Smith, *Fundamentals of Fourier transform infrared spectroscopy*, CRC press, 2011.
- [30] N. Rahimi, R. Karimzadeh, Catalytic cracking of hydrocarbons over modified ZSM-5 zeolites to produce light olefins: A review, *Appl. Catal. A Gen.* 398 (2011) 1–17.  
<https://doi.org/10.1016/j.apcata.2011.03.009>.
- [31] S.L. Wong, N. Ngadi, T.A.T. Abdullah, I.M. Inuwa, Conversion of low density polyethylene (LDPE) over ZSM-5 zeolite to liquid fuel, *Fuel.* 192 (2017) 71–82.  
<https://doi.org/10.1016/j.fuel.2016.12.008>.
- [32] A.R. Songip, T. Masuda, H. Kuwahara, K. Hashimoto, Production of High-Quality Gasoline by Catalytic Cracking over Rare-Earth Metal Exchanged Y-Type Zeolites of Heavy Oil from Waste Plastics, *Energy and Fuels.* 8 (1994) 136–140.  
<https://doi.org/10.1021/ef00043a023>.
- [33] G. Protić-Lovasić, N. Jambrec, D. Deur-Siftar, M. V. Prostenik, Determination of catalytic reformed gasoline octane number by high resolution gas chromatography, *Fuel.* 69 (1990) 525–528. [https://doi.org/10.1016/0016-2361\(90\)90328-N](https://doi.org/10.1016/0016-2361(90)90328-N).
- [34] J. Weitkamp, Zeolites and catalysis, *Solid State Ionics.* 131 (2000) 175–188.  
[https://doi.org/10.1016/S0167-2738\(00\)00632-9](https://doi.org/10.1016/S0167-2738(00)00632-9).
- [35] Y.H. Seo, K.H. Lee, D.H. Shin, Investigation of catalytic degradation of high-density polyethylene by hydrocarbon group type analysis, *J. Anal. Appl. Pyrolysis.* 70 (2003) 383–398. [https://doi.org/10.1016/S0165-2370\(02\)00186-9](https://doi.org/10.1016/S0165-2370(02)00186-9).

- [36] W. Ding, J. Liang, L.L. Anderson, Thermal and catalytic degradation of high density polyethylene and commingled post-consumer plastic waste, *Fuel Process. Technol.* 51 (1997) 47–62. [https://doi.org/10.1016/S0378-3820\(96\)01080-6](https://doi.org/10.1016/S0378-3820(96)01080-6).
- [37] Y. Uemichi, M. Hattori, T. Itoh, J. Nakamura, M. Sugioka, Deactivation Behaviors of Zeolite and Silica-Alumina Catalysts in the Degradation of Polyethylene, *Ind. Eng. Chem. Res.* 37 (1998) 867–872. <https://doi.org/10.1021/ie970605c>.
- [38] S. Senger, L. Radom, Zeolites as transition-metal-free hydrogenation catalysts: A theoretical mechanistic study, *J. Am. Chem. Soc.* 122 (2000) 2613–2620. <https://doi.org/10.1021/ja9935097>.
- [39] P. Castaño, G. Elordi, M. Olazar, A.T. Aguayo, B. Pawelec, J. Bilbao, Insights into the coke deposited on HZSM-5, H $\beta$  and HY zeolites during the cracking of polyethylene, *Appl. Catal. B Environ.* 104 (2011) 91–100. <https://doi.org/10.1016/j.apcatb.2011.02.024>.
- [40] A. Marcilla, M.I. Beltrán, R. Navarro, Study of the deactivation process of HZSM5 zeolite during polyethylene pyrolysis, *Appl. Catal. A Gen.* 333 (2007) 57–66. <https://doi.org/10.1016/j.apcata.2007.09.004>.

